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Fabrication of Barium Strontium Titanate ($Ba_{1-x}Sr_xTiO_3$) Films Used for Bio-inspired Infrared Detector Arrays

by Kimberley A. Olver

ARL-TR-6112 **September 2012**

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED (From - To)
September 2012	Final	

4. TITLE AND SUBTITLE
Fabrication of Barium Strontium Titanate (Ba1–xSrxTiO3) Films Used for Bio-inspired Infrared (IR) Detector Arrays

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Kimberley A. Olver

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory
ATTN: RDRL-SEE-I
2800 Powder Mill Road
Adelphi, MD 20783-1197

8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-TR-6112

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
Through a three-way collaboration between the Institute for Collaborative Biotechnologies (ICB) at the University of California, Santa Barbara; The Aerospace Corporation; and the U.S. Army Research Laboratory, we investigated the use of a pyroelectric perovskite based material for a novel two-dimensional uncooled infrared focal plane array. Barium strontium titanate (BSTO) was chosen by the ICB as the perovskite material to be used due to its stable nanocrystals, which would allow a high quality, homogenous, crack-free film to be dispersed onto sensor readouts. This ferroelectric ceramic material, once transformed into the pyroelectric crystalline form, would be used as the active material in thermal imaging devices. An in-house process for the film deposition was developed for this purpose.

15. SUBJECT TERMS
Barium Strontium Titanate, 2-dimensional IR FPA, Perovskite, uncooled IR detectors

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Kimberley A. Olver
Unclassified	Unclassified	Unclassified	UU	18	19b. TELEPHONE NUMBER (*Include area code*) (301) 394-2048

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

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1. Introduction

The goal of this three-way collaboration between the Institute for Collaborative Biotechnologies (ICB) at the University of California, Santa Barbara, The Aerospace Corporation, and the U.S. Army Research Laboratory (ARL) was to design, fabricate, and characterize device arrays consisting of a thin film of pyroelectrically active crystalline ceramic barium strontium titanate (BSTO), which would be used as the active device layer in Army applications requiring uncooled infrared (IR) detectors. BSTO is a ferroelectric material having a perovskite structure (*1*). The benefits of this new material system would be an uncooled, lighter weight detector; a faster, more simplistic fabrication process; and therefore, a shorter turnaround time at lower production costs. The ICB developed the process used to create a nanoparticulate solution of BSTO. The pyroelectric perovskite based solution was made through a catalytic, kinetically controlled growth of crystalline nanoparticles using a novel vapor diffusion sol-gel process (*2*). The Army's original objective was to characterize already deposited films of this perovskite material, both before and after the films had gone through a laser induced transformation into the pyroelectrically active crystalline phase. Due to problems with the initial films we received, a new in-house procedure for depositing the films onto silicon substrates was developed (figure 1).

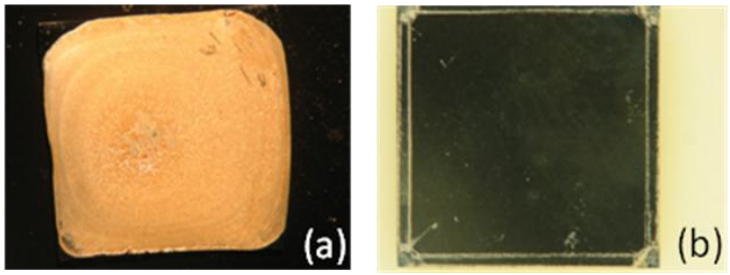

Figure 1. Images of BSTO film as received (a), and produced in-house (b).

This new procedure involved spin-casting the BSTO solution onto silicon substrates and then curing the resultant film in a furnace at elevated temperatures. After receiving the BSTO solution at ARL, the films were deposited onto metalized silicon square substrates using the developed spin-cast method, baked on a vacuum hot plate, and then cured in a furnace at a relatively high temperature. Metal contacts were lithographically patterned on the top surface of the cured film. The substrate was epoxied into a leadless chip carrier (LCC) package, and wirebonds were attached to the top and bottom metal contacts of the device.

Initially, the cured films were electrically characterized for their dielectric properties by measuring their temperature and frequency dependent capacitance. During baseline electrical testing, it was found that direct wirebonding to the top contacts were creating short circuits. This was attributed to the thinness of the film; therefore, thicker films were produced by increasing

the number of spin-cast/bake cycles. Additional electrical testing showed the films to be too thin for measuring the resistance (short circuits were resulting), so even thicker films were produced by again increasing the number of spin-cast/bake cycles. The thicker (approximately 1 micron) films were evaluated and found to be continuous with no cracking. After electrically characterizing the BSTO films, they were sent to The Aerospace Corporation where they underwent a laser-induced phase transformation into the pyroelectrically active crystalline phase. A direct-write, digitally scripted laser pulse was used to define pixels/arrays and convert the material from its inactive cubic phase to the pyroelectrically active tetragonal phase within the film. This technique was developed at The Aerospace Corporation.

In order to create a hybridized device system out of the transformed crystalline material, we designed an array layout for the films based on already existing electrical readouts, allowing The Aerospace Corporation to pixilate the material into an array pattern we were already familiar with and that we could integrate directly onto our readouts. The Aerospace Corporation wrote a laser-pulse script to match this array pattern.

Post phase conversion, the films were returned to ARL where they were processed into individual 8x8 device arrays, tested, flip chip bonded to the corresponding readouts, packaged, and tested again.

2. Procedure

Figure 2 describes the steps taken for the BSTO film fabrication, pixilation, and device hybridization.

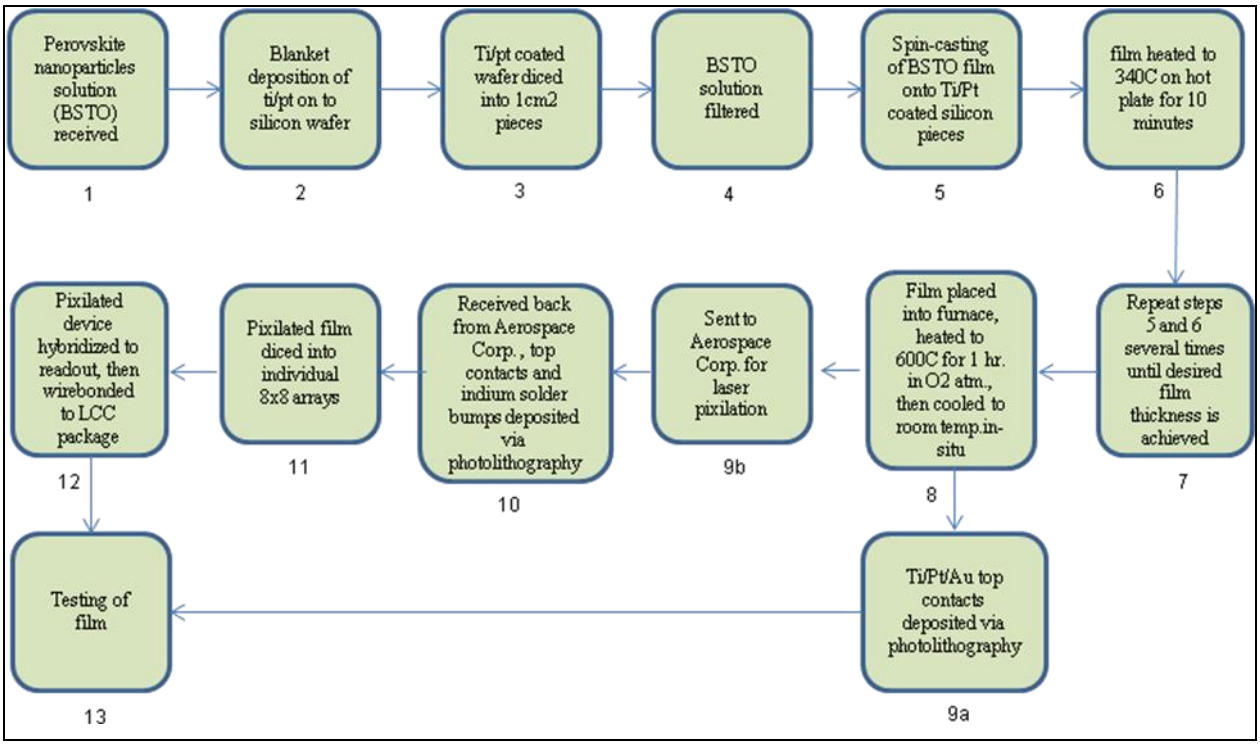

Figure 2. Flow chart of BSTO device process.

2.1 Preparation of Silicon Substrates and Formation of Bottom Electrical Contacts

A new 3-inch silicon wafer was metalized in a vacuum electron-beam evaporator with 300 angstroms (Å) of titanium followed by 1000 Å of platinum. This Ti/Pt metallization formed what was to be the bottom contact for our films. The wafer was then coated with a temporary protective coating material, Shipley-Microposit surface coating material FSC-M, baked in a vacuum oven at 95 °C for 30 min, and then mechanically diced into 1 cm^2 pieces. The FSC-M was removed from the diced substrates using acetone, followed by isopropyl and deionized (DI) water then blown dry with nitrogen (N_2) gas.

2.2 Fabrication of BSTO Films on Substrates

The as-received solution used for making the BSTO films was prepared by suspending 1.2 g of BSTO nanoparticles in 20 ml of hexane and 4.7 ml of oleic acid. The particles were precipitated with the addition of ethanol and redispersed into 20 ml of hexane. This last step removed the excess oleic acid (K. Niesz, private communication).

The first attempt at creating an in-house BSTO film used the drop-cast method in which a drop of as-received solution was placed in the center of a substrate, and the substrate placed on a hot plate at 300 °C for 1 min. The resulting film was examined and found to be flakey, uneven, and very rough due to large crystalline particulates in the solution. This film was found to be unsuitable for photolithography. The spin-cast process was therefore developed for fabricating the films on the substrates. Because the bottom contact of our device was a deposited

metallization of Ti/Pt on the silicon substrate, a small piece of Kapton tape was used to mask off a corner of the substrate prior to applying the BSTO solution. A substrate was placed on a vacuum chuck of a Headway photoresist spinner, the spinner was started at a spin speed of 1850 rpm, and two to three drops of the as-received solution placed into the center of an already spinning substrate. When the spin cycle ended (30 s), the now-coated substrate was placed onto a hot plate at 300 °C for 1 min. At this point the Kapton tape was removed. These films were smoother and more evenly distributed, but were still rough due to the crystalline particulates in the solution, and photolithography proved very difficult due to this surface roughness. In order to create a smooth film, the BSTO solution was filtered through a Whatman 0.2 µm nylon filter using a 5 ml disposable syringe (*3*, *4*). A syringe was filled half way with the BSTO fluid. The filter was coupled to the bottom of the syringe, the solution was pressed through the filter, and the resulting fluid was captured in a small glass container (figure 3).

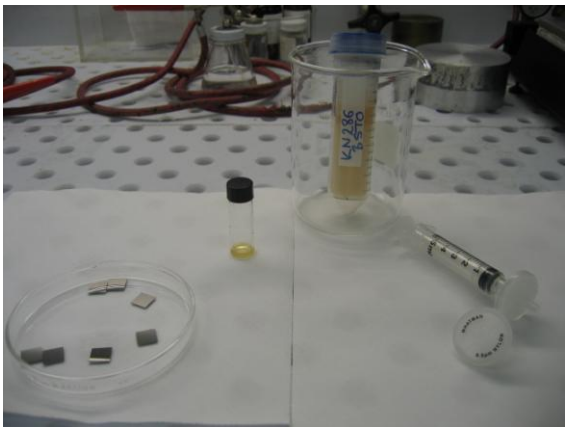

Figure 3. BSTO filtration setup.

This filtered fluid was then spin-cast onto a substrate at spin speeds of 1850 rpm/20 s followed by 2000 rpm/10 s. This spinning technique again involved dropping two to three drops of the fluid onto the center of the spinning substrate. The resulting BSTO film was then hotplate baked at 340 °C for 10 min. Baking the film at this point was to drive off any remaining solvent. This procedure was repeated for a total of three times resulting in a smooth, crack-free film about 300 nm thick. In order to cure completely and eliminate an observed hydroxyl defect (*5*, *7*), the films were then placed into a quartz tube furnace and baked at 600 °C for 1 hr in an oxygen atmosphere (figure 4). The films were cooled in the furnace to room temperature before removing.

Figure 4. Three zone furnace used for curing BSTO films.

This new BSTO film was now smooth enough to perform photolithography on. Using standard photolithography techniques, a metallization layer of Ti/Pt/Au was e-beam deposited and a post-evaporation metal lift-off performed to create a top contact pattern. The uncoated corner area of the substrate was the bottom contact.

2.3 Characterization

Using probe tips connected to a parameter analyzer, the films were electrically tested and found to be appropriately resistive for producing devices. But, in attempting to test the electrical resistance of these films, which had been mounted into a LCC (figure 5), it was found that although using probe tips to test the films worked well, the physical act of wirebonding to the top contact somehow damaged the film underneath the metal. It was decided that a thicker film would remedy this. So the spin cast/hot plate bake cycle was repeated for a total of eight times, producing a 1-micron-thick film. This film was found to be continuous with no cracking. Due to the concerns of direct wirebonding to the top contacts, it was decided that flip-chip hybridization was a good alternative to this.

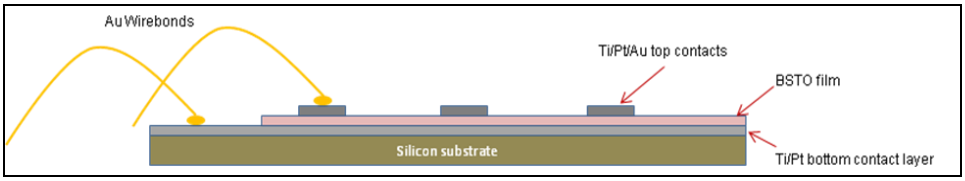

Figure 5. Diagram of BSTO film on silicon substrate with wirebonds attached.

After curing the films and cooling them in-situ, the films were removed from the furnace and sent to The Aerospace Corporation for laser pixilation. The Aerospace Corporation used a laser-

pulsed scripting technique they developed to transform the BSTO film into its pyroelectrically active crystalline form. The result was a material phase conversion in specific areas. We designed the pattern for the laser pixilation, allowing us to use an already existing readout for hybridization. Each laser pixilated film produced approximately 16 individual 8x8 device arrays.

Once back at ARL, a photolithography/metallization process was performed to create top electrical contacts on the arrays. However, before the top contact could be deposited, the BSTO film at the bottom row of pixels needed to be removed down to the Ti/Pt layer. This bottom row of pixels was removed by hand, using a microscope and a very small hand-held scraping tool. This row would form the electrical ground (common) for our devices. Micro Chemicals AZ 5214 E image reversal photoresist was used to pattern the 8x8 arrays corresponding to the laser defined pixels. The individual pixel size was 100 square microns. Top contact metal pads were e-beam deposited onto the area of pixilation on the film. A deposition of 350 Å of Ti followed by 400 Å of Pt then 2500 Å of Au was performed. After being removed from the evaporator, a liftoff of excess metal was completed (figure 6).

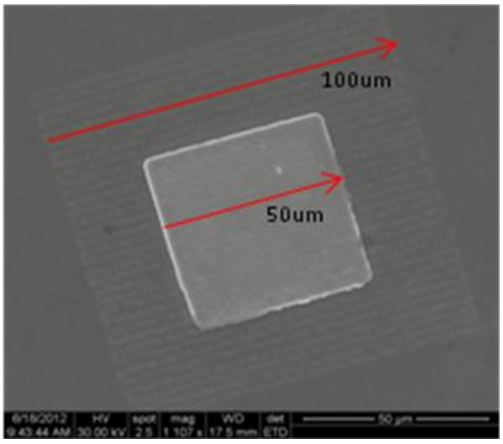

Figure 6. SEM image of 100 μm^2 area where BSTO film has been laser-pixilated. 50-μm^2 contact pad on top of laser scripted pixel.

Prior to the indium bump lithography, these arrays were temporarily epoxied into a 68 pin (LCC). Individual pixels were wirebonded to connections on the LCC, and measurements of the frequency and temperature dependent changes in current and capacitance of the transitioned BSTO film were taken. After these measurements, the device arrays were prepared for hybridization.

2.4 Hybridization

Indium solder bump technology is a unique process used mainly for flip-chip hybridization of semiconductor components. Flip Chip hybridization is an electrical and mechanical interconnect process which eliminates the need for peripheral wirebonding. Also known as direct chip attach (DCA), it allows for lower lead resistance compared with wirebonding due to very short

conductive bonds (*6*). In order to hybridize our laser-pixilated 8x8 arrays onto silicon readouts, indium solder bumps were lithographically fabricated onto the metal top contacts. MicroChemicals AZ #4620 positive photoresist was used for the lithography of the indium solder bumps. A vacuum-thermal evaporation of 300 Å chromium for metal adhesion followed by several microns (~5 µm) of indium was performed. A metal lift-off of the excess indium metal produced the indium bumps (figure 7).

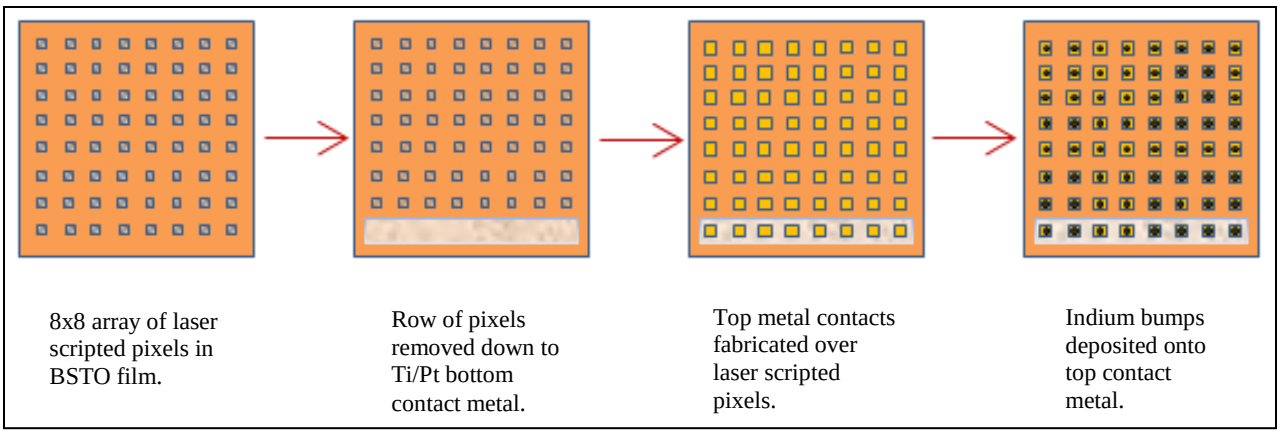

Figure 7. Fabrication of indium solder bumps on a laser-pixilated 8x8 array.

The now-metalized film was again spin-coated with FSC-M and baked at 95 °C for 30 min prior to being mechanically diced into individual 8x8 arrays (figure 8).

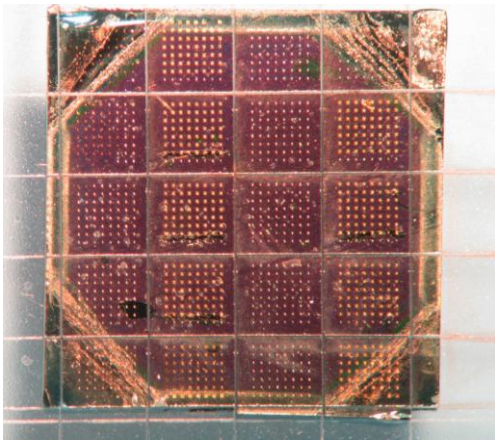

Figure 8. Image of diced, laser scripted BSTO film.

After dicing, the individual arrays were removed from the dicing tape, cleaned in acetone followed by isopropyl, rinsed in DI water, and blown dry with N_2 gas. After this complete cleaning, the individual arrays were ready to be hybridized to individual silicon readouts using a Research Devices, Inc. M8-A flip-chip bonder (figure 9). Six hundred grams of force was used in hybridizing the BSTO device array to the readout. Because indium bumps were deposited on both the devices and the readout, heat was not needed in the hybridization process. The now-hybridized array/readout assembly was epoxied into a 68-pin LCC and the readout bonding pads

were wirebonded (figure 10). This hybridization process and follow-up wirebonding allowed for each individual device pixel to be electrically characterized without having to wirebond to the device, which we had found could damage the film. The results of these tests were reported elsewhere (*7*).

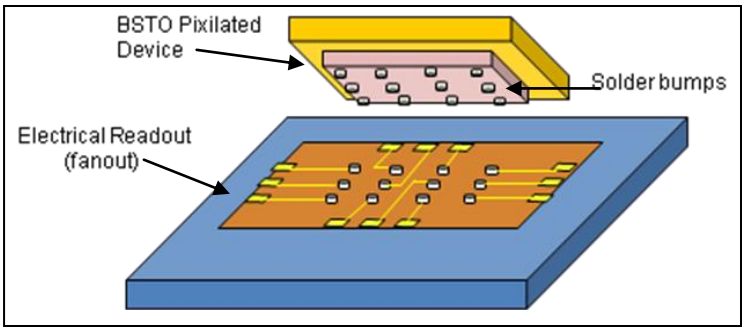

Figure 9. Diagram of hybridization between BSTO device array and silicon readout.

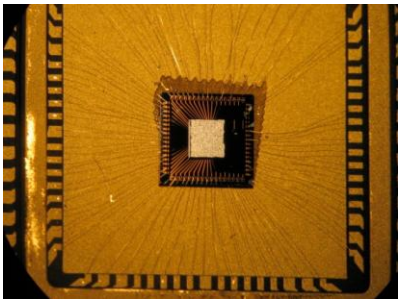

Figure 10. Image of hybridized BSTO device to silicon readout. The assembly is epoxied and wirebonded into an LCC.

3. Results/Conclusion

BSTO is a ferroelectric ceramic material with a perovskite structure, which, when transformed (phase converted) from its cubic phase to its tetragonal phase, becomes a material that is pyroelectrically active. This electrical ceramic has the potential to be used as the active material in two-dimensional thermal imaging devices. Our goal was to fabricate thin films from the BSTO solution and process these films into devices. Creating a smooth film out of the BSTO solution proved to be a challenge. Initially, a drop-cast method of film deposition was used, but the film quality from these first attempts was poor. In order to make a BSTO film that could be fabricated into working device arrays, several new processes were developed. Using solution filtration, a spin-cast method of deposition and subsequent temperature and time dependent curing techniques, we were able to fabricate dense, smooth 1 µm thick BSTO films. Using a pulsed laser scripting program written and executed by The Aerospace Corporation, a laser-

induced phase transformation converted the BSTO from its inactive cubic phase to its pyroelectrically active tetragonal phase. The script used was an 8x8 pixel array design corresponding to our already existing readouts. These patterned films were now able to be fabricated into two-dimensional, 8x8 pixel arrays via traditional photolithography procedures. The device arrays were electrically characterized, measuring for a pyroelectric effect, then diced and hybridized to the pre-existing readouts using indium bump technology, and characterized again.

Frequency and temperature-dependent capacitance are the main factors used in measuring the pyroelectricity of a material. Both of these measurements were performed on our devices. We did not observe a pyroelectric effect in our devices. However, we were able to measure uniform capacitance from device to device in the thicker films, both before and after flip-chip hybridization. This would indicate that with more fundamental research, developing this perovskite material into a novel uncooled, low-cost, two-dimensional IR focal plane array would be possible – benefiting the Army's thermal imaging capabilities.

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List of Symbols, Abbreviations, and Acronyms

Å	angstroms
Au	gold
ARL	U.S. Army Research Laboratory
BSTO	barium strontium titanate
DCA	direct chip attach
DI	deionized
ICB	Institute for Collaborative Biotechnologies
IR	infrared
LCC	leadless chip carrier
N_2	nitrogen
Pt	platinum
Ti	titanium

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